

# Effect of Sulfur Concentration on the Morphology of Carbon Nanofibers Produced from a Botanical Hydrocarbon

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**Abstract** Carbon nanofibers (CNF) with diameters of 20–130 nm with different morphologies were obtained from a botanical hydrocarbon: Turpentine oil, using ferrocene as catalyst source and sulfur as a promoter by simple spray pyrolysis method at 1,000 °C. The influence of sulfur concentration on the morphology of the carbon nanofibers was investigated. SEM, TEM, Raman, TGA/DTA, and BET surface area were employed to characterize the as-prepared samples. TEM analysis confirms that as-prepared CNFs have a very sharp tip, bamboo shape, open end, hemispherical cap, pipe like morphology, and metal particle trapped inside the wide hollow core. It is observed that sulfur plays an important role to promote or inhibit the CNF growth. Addition of sulfur to the solution of ferrocene and turpentine oil mixture was found to be very effective in promoting the growth of CNF. Without addition of sulfur, carbonaceous product was very less and mainly soot was formed. At high concentration of sulfur inhibit the growth of CNFs. Hence the yield of CNFs was optimized for a given sulfur concentration.

**Keywords** Carbon nanofiber · Spray pyrolysis method · Botanical hydrocarbon · Scanning electron microscopy · Transmission electron microscopy

## Introduction

Carbon nanofibers have attracted the tremendous attention because of their potential applications in the field of science and technology. They can be used as in hydrogen storage materials [1], filler for polymer composites [2], field emission devices, sensors, fuel cells, and supercapacitors [3]. Therefore, extensive effort was made to develop CNFs by different methods using different metal catalyst (Fe, Co, Ni, Cu, etc.) and different carbon feedstock. However, most of the work was done with zero valence iron compounds, such as  $\text{Fe}(\text{C}_5\text{H}_5)_2$  or  $\text{Fe}(\text{CO})_5$  in order to favor and control the catalyst particle size [4] to grow selective nanofiber. There are different kinds of carbon nanofiber viz. platelet carbon nanofiber, fishbone carbon nanofiber, ribbon nanofiber, herringbone nanofiber, stacked cup carbon nanofiber, etc. They are classified according to their arrangement of graphene layer with respect to the fibril axis.

Carbon fibers are mainly synthesized by chemical vapor deposition method from a carbon source using transition metal as catalyst. The carbon nanofibers seem to form either in the vapor phase [5, 6] or over catalyst deposited on supported material [7, 8]. A sulfur compound (elemental sulfur, hydrogen sulfides, thiophene) is essential with metal catalyst to promote the catalytic growth for CNFs formation [6, 9]. It helps to increase the reaction kinetics which reduces the soot formation and leads to formation of thickened carbon nanofiber [6]. Small amount of such impurity helps to produce fibers of reasonable quality and

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good yields. In an earlier study it was observed that without any hydrogen sulfides in the feedstock, a negligible amount of fibers formed and the major products was soot [9]. Sulfur plays an important role for the formation of CNFs as it liquefies iron particle that enhances CNFs formation. This liquefaction considerably increases the formation of CNFs by VLS process, due to formation of eutectic between iron and iron-sulfur compounds at 988 °C [6].

To date, various petroleum products, such as methane [10], xylene [11], benzene [12], etc., are in practice to synthesize CNFs. However, in view of foreseen crisis of fossil fuels in the near future, it is desirable to look for alternative carbon feedstock to synthesize this kind of nanomaterials. Turpentine oil is very effective precursor to synthesize CNFs. Turpentine oil is a botanical hydrocarbon and derived from oleoresin of pinus species. It is found mainly in most parts of Asia, Europe and USA. This precursor is generally used in paints and varnishes. It is mainly composed of  $\alpha$ -pinene and  $\beta$ -pinene with a boiling point of 170 °C. This precursor is very cheap and eco-friendly. One of the most advantages of this precursor is that there is no chance of crisis of this carbon feedstock in near future. This precursor has shown potential of producing vertically aligned carbon nanotubes [13, 14], multi-walled and single-walled carbon nanotubes [15, 16].

In this contribution, we have studied the effect of sulfur concentration on the morphology of carbon nanofibers with the use of natural precursor: Turpentine oil, a carbon feedstock, ferrocene as catalyst and sulfur as promoting agent. This is the first report of synthesis of carbon nanofiber from a botanical hydrocarbon: Turpentine oil using sulfur as a promoter by a simple, viable, and cost-effective spray pyrolysis method.

## Experimental

### Production of Carbon Nanofibers

Carbon nanofibers were produced in a horizontal furnace, using ferrocene as a catalyst, turpentine oil as hydrocarbon feedstock and sulfur as a promoter at 1,000 °C by spray pyrolysis method. The only variable in our experiment was the concentration of sulfur, keeping other experimental parameters (temperature, flow rate of gas, flow rate of solution, and ferrocene concentration) same. Detail information of this spray pyrolysis system was described elsewhere [13]. A quartz tube of 1-m length and 25-mm diameter which is serving as spray pyrolysis reactor was kept inside one horizontal furnace. The inlet of the quartz tube was attached with the spray nozzle that helps to spray the precursor solution containing mixture of turpentine oil, ferrocene and small amount of sulfur by nitrogen gas.

The outlet of the tube was connected with the water bubbler. At the initial stage, nitrogen gas was passed for a few minutes to expel out atmospheric air from the tube. The furnace was then switched on with a desired deposition temperature (1,000 °C). When the furnace attains the desired temperature, precursor solution was sprayed through spray nozzle by the help of nitrogen gas. The flow rate of nitrogen gas was 2.5 L/min and deposition time was lasted for 5 min. During the deposition process, the catalyst particles decomposed and formed sulfur contaminated iron nanoparticles and CNFs started to grow. After 5 min, furnace was cooled down naturally to room temperature. The CNFs mainly deposited on the inner wall of the exit part of the reactor which was easily peeled off and used for characterization.

### Characterization Techniques

Several characterization techniques (SEM, TEM, Raman spectroscopy, TGA/DTA, and BET surface area) were employed on the as-grown samples. The morphology of the as-grown CNFs was analyzed by electron microscopy. Scanning electron microscopy (SEM) studies were carried out by SEM (Hitachi S-3000H, scanning electron microscope). Transmission electron microscopy was performed by HITACHI, HF-2000 with an acceleration voltage 200 kV. For TEM observation, the sample was prepared by sonication of the as-synthesized product in methanol, and a few drops of the resultant suspension were put onto a holey carbon TEM grid. TGA/DTA was performed with DTG-60, Shimadzu, and TA-60 WS thermal analyzer with a heating rate of 10 °C/min with 100 sccm/min flow of air. Raman spectroscopy (JASCO, NRS-1500W) was measured with an excitation wavelength of 532 nm from a green laser with typical acquisition time 30 s. The microporous properties of the samples were determined by SHIMADZU Tristar 3000 to get the BET surface area of the as-grown CNFs.

## Results and Discussions

### SEM Analysis

Figure 1a–d shows the SEM images of CNFs prepared at different sulfur concentrations varies from 10.5 to 40 at.%. These images clearly show that the morphology of product is strongly influenced by the atomic ratio of Fe and S. At 10.5 and 40 at.% of Sulfur concentration, the density of as-grown fiber is lower compared to that of 21 and 31.5 at.% sulfur grown CNFs. Figure 1b and c depict the SEM images of as-prepared CNFs grown by using 21 and 31.5 at.% which indicates that the amount of free soot is very less and

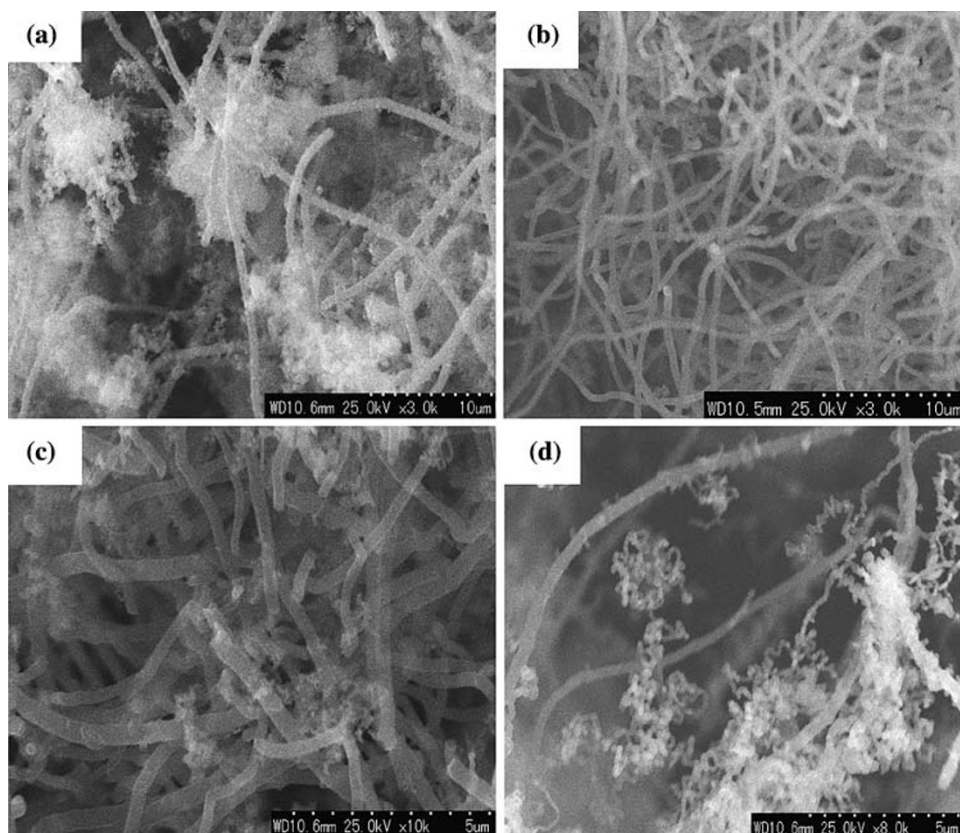
diameter of as-prepared CNFs is almost uniform. Moreover, it can be observed that 21 and 31.5 at.% sulfur grown CNFs have a smooth surface. However, at 10.5 at.% of sulfur grown CNFs, soot are observed in large extent. The nanofibers grown from 40 at.% of sulfur, the density is very less and fibers are quite straight. This might be due to poison of the iron catalyst which leads to product of low yield.

### TEM Analysis

TEM images of as-prepared CNFs grown from 21 to 31.5 at.% of sulfur concentration are shown in Fig. 2. It is revealed that decomposition of turpentine oil generates different kinds of CNFs viz. bamboo like, tubular and sharp tip geometrical pattern at different sulfur concentration. It can be clearly seen from TEM images that at lower sulfur concentration, the as-grown CNFs are relatively thicker than the CNFs prepared at high sulfur concentration. It is very clear from TEM analysis that as-grown fibers are well-graphitized and amorphous carbon coating on the surface of the CNFs is very less which is also confirmed from TGA/DTA analysis. The structure of CNFs with 31.5 at.% of sulfur have variable diameter (from 80 to 112 nm) along graphene layer direction as shown in Fig. 2a. Some of the CNFs are bamboo like with some transverse bridge forming compartment (Fig. 2b and c) and

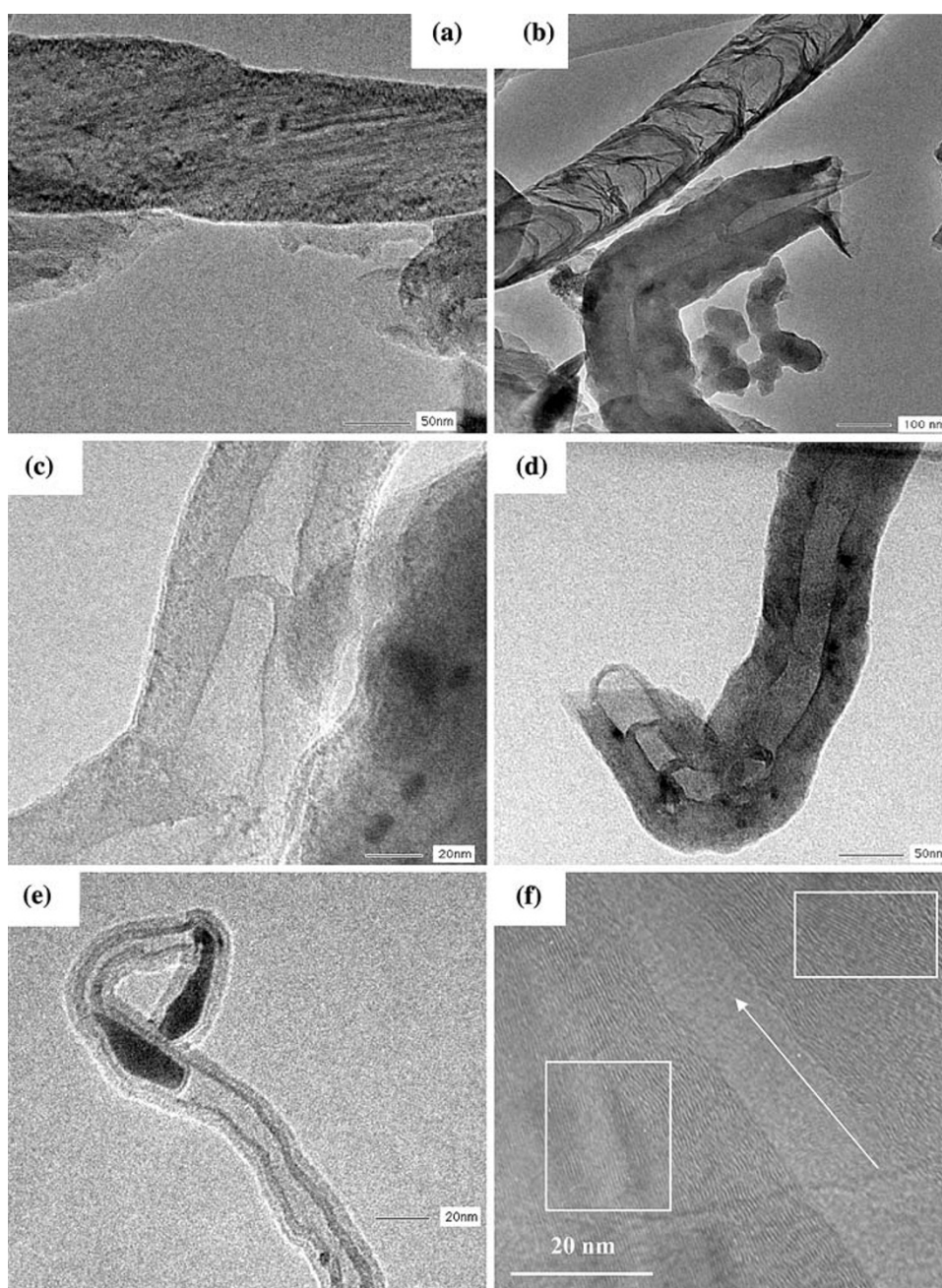
very few CNFs contain sharp tip (Fig. 2b). Such CNF with sharp tip have high expectation for enhanced of field electron emission. Figure 2d shows as-grown nanofibers with hemispherical cap. In Fig. 2e, the catalyst particles were observed at the tip and inside the hollow channel of CNFs. At the initial stage of the fiber growth process the catalyst particle flow out of their molten state lead to the formation of internal hollow channel. Furthermore, near to the tip of the fiber, molten catalyst particle has been fragmented into two parts. Both the fragments have tapered their bodies so as to grow hollow CNFs in between themselves. In Fig. 2f, two kinds of graphene arrangement have been observed. Near to the main fiber axis (shown by arrow head), graphene sheets are parallel whereas, graphene alignment away from the main axis angled by 50–60°, shown by rectangle area. In some cases metal particles were also observed inside the hollow core of CNFs and core diameter (25 nm) is almost similar to the metal particle size (Fig. 2g). Here, a few metal particles sit over the fiber and they are deactivated due to the small layer of carbon coating. Some of the metal particles remain their activity alive which is responsible for short in-situ fiber growth over main fiber platform (Fig. 2h). The graphene sheets of this short nanofiber are parallel to the main fiber graphene sheet. Ellipsoid catalyst particle was found at the tip of this fiber and the diameter of the CNF seems to be

**Fig. 1** SEM images of as-grown CNFs prepared at different sulfur concentration (a) 10.5 at.% sulfur (b) 21 at.% sulfur (c) 31.5 at.% sulfur (d) 40 at.% sulfur





**Fig. 2** TEM pictures of 31.5 at.% sulfur grown CNFs (a) CNF with a wide and variable diameter (b) bamboo-shaped and sharp tip CNF (c) CNF with transverse bridge compartment (d) CNF with hemispherical cap (e) a 25 nm CNF with metal particle at the tip and hollow channel of CNF (f) two kinds of graphene arrangement in CNFs (g) a 47 nm CNF with metal particle inside the hollow core (h) a short fiber grown over a fiber (i) open ended CNF with diameter of 75 nm (j) CNF with amorphous carbon coating (k) general overview of 21 at.% sulfur grown CNF (l) wide CNF, grown using 21 at.% of sulfur



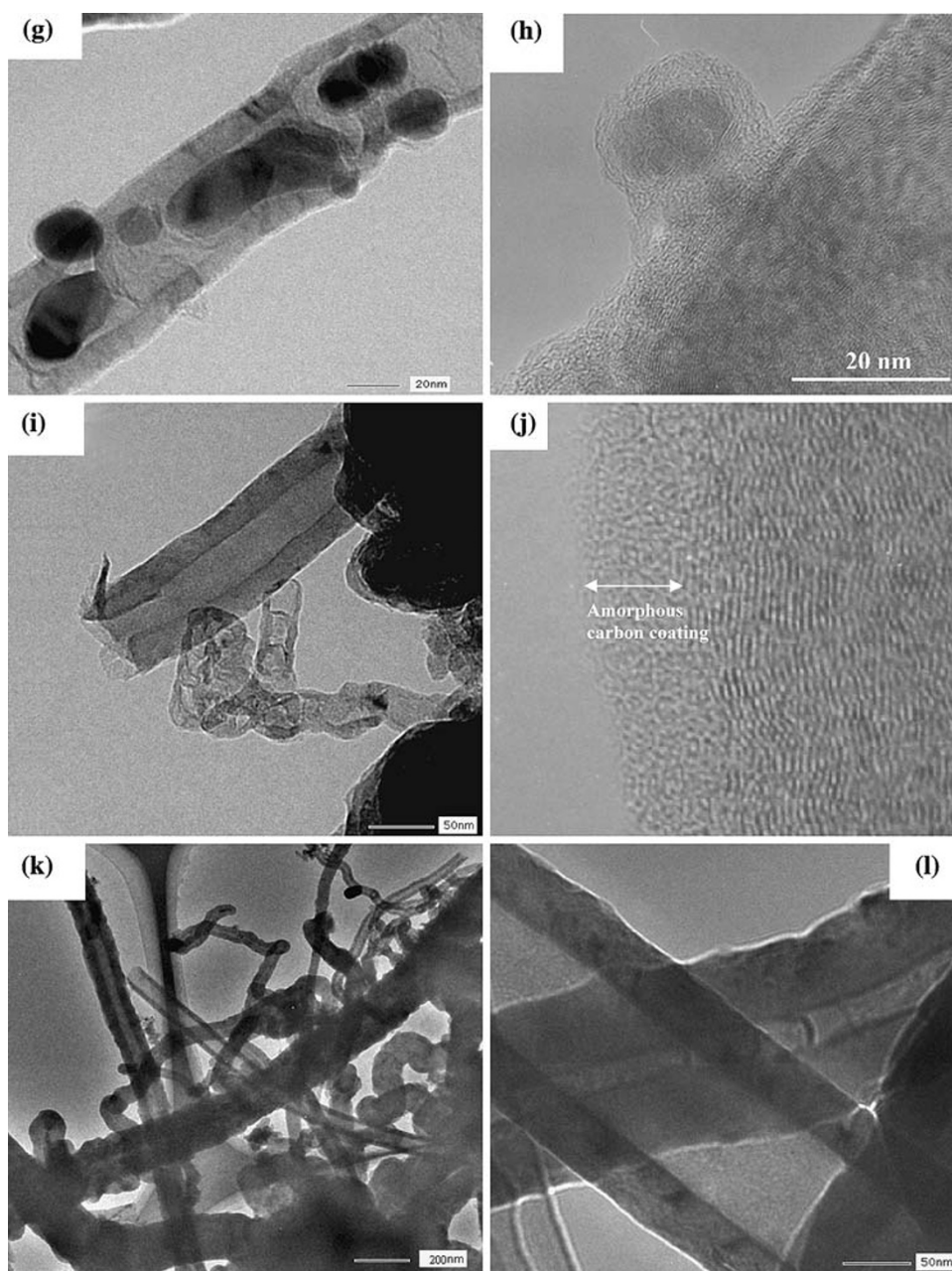
determined by the shape and size of the catalyst particle, as shown in Fig. 2h. Very few nanofibers are open ended with outer diameter of 70 nm (Fig. 2i). At lower sulfur concentration (21 at.%), we got mostly pipe like structure with open end and hollow core (Fig. 2k and l).

### Raman Spectroscopy

Raman spectroscopy is widely used to characterize the structural and phase disorder information in carbon related material. Figure 3 shows Raman spectroscopy of the as-grown CNFs, prepared at different sulfur concentration

by using a green laser with an excitation wavelength of 532 nm and power of 14.4 mW in a range of Raman shift from 1,100 to 1,800  $\text{cm}^{-1}$ . Each spectrum was performed with 30 s acquisition time with an illumination spot size of 1  $\mu\text{m}$ . In the Raman-shift range (1,100–1,800  $\text{cm}^{-1}$ ), two peaks are observed at approximately 1,345 and 1,573  $\text{cm}^{-1}$  region, which corresponds to the D- and G-band, respectively. The G-band is attributed to the Raman active  $E_{2g}$  in-plane oscillation mode and D-band corresponds to the  $A_{1g}$  in-plane breathing vibration mode due to structural defects in the graphite crystal. The rather sharp D and G band, together with the evident high-frequency shoulder of

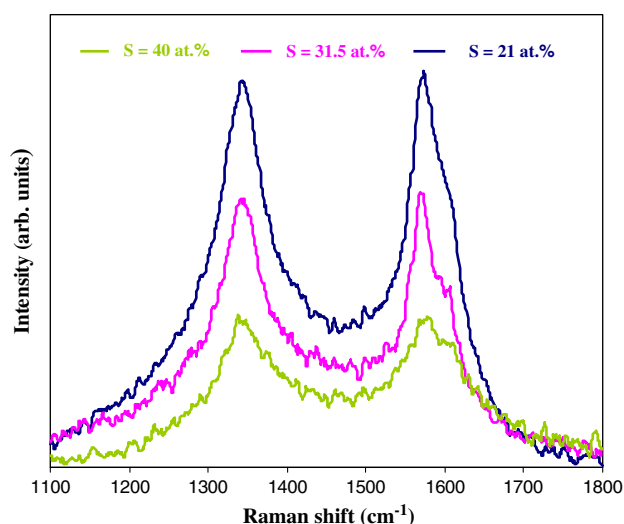
Fig. 2 continued



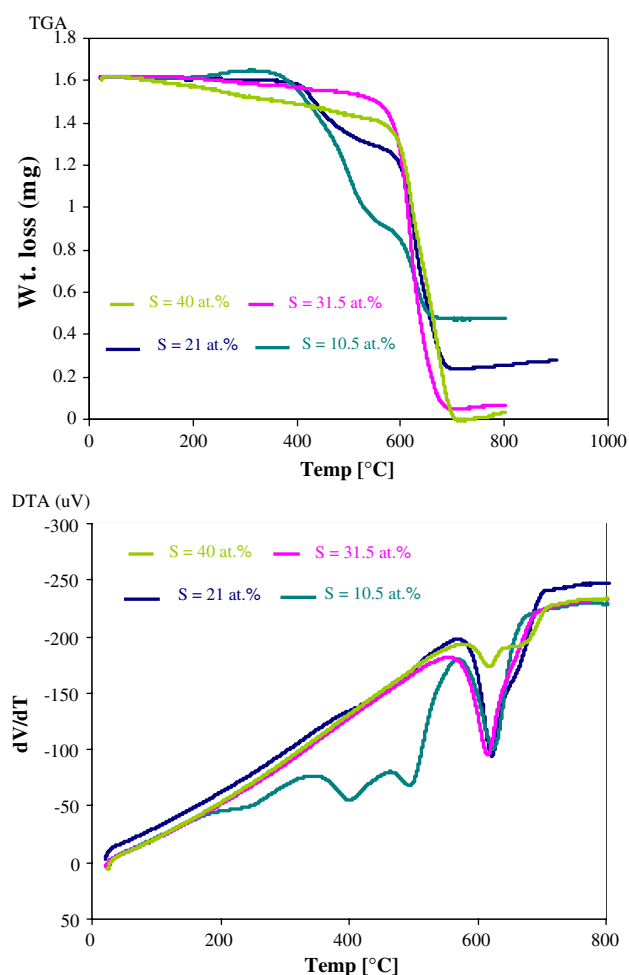
the G peak, indicate the order and crystallinity of the CNFs [17, 18]. Relative intensity ratio of D and G-peaks ( $I_d/I_g$ ) is a measure of amount of disorder in the CNFs. It is well known that low intensity of D- band relative to G-band indicates a low amount of amorphous carbon or lower defect in the CNFs. The  $I_d/I_g$  value is found to be  $\sim 1$  for CNFs prepared at different sulfur concentration, indicating a large quantity of defects in the CNFs structure. The defects in the as-grown CNFs are due to the presence of amorphous carbon coating which is shown in Fig. 2j.

#### Thermogravimetric Analysis of As-grown CNFs

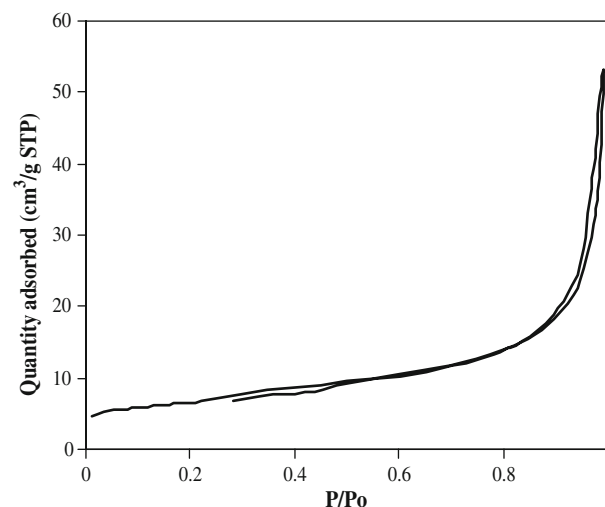
Thermogravimetric analysis and corresponding DTA curves of as-grown nanofibers are shown in Fig. 4. Detail study shows that all the fibers grown at different sulfur concentration mostly show their oxidation temperature at around 620 °C. This temperature is decomposition temperature of as-prepared carbon nanofibers. The apparent mass loss below 400 °C is due to mainly oxidation of soot. At very low sulfur concentration (10.5 at.%) we have got some oxidation peaks at 400 and 498 °C. We assume that



**Fig. 3** Raman spectroscopy of carbon nanofibers prepared at different sulfur concentration



**Fig. 4** Thermogravimetric analysis and corresponding derivative profile of as-prepared CNFs



**Fig. 5** Nitrogen adsorption isotherm of 31.5 at.% sulfur grown CNF

these peaks are mainly responsible for low diameter nanofiber. With increasing sulfur concentration from 21 to 31.5 at.%, DTA maxima shifted towards lower value. This shift of DTA maxima by changing the sulfur concentration from 21 to 31.5 at.%, is attributed to the lower diameter nanofibers, that has been observed in TEM analysis. The high diameter and less deformity in fibril structure are less susceptible to oxidize.

#### Surface Characteristic Studies of As-grown CNFs

In order to determine the effective surface area of as-grown nanofibers, nitrogen cryo-adsorption isotherm was carried out. Figure 5 shows the nitrogen cryo-adsorption isotherm of CNFs prepared from 31.5 at.% of sulfur concentration. Monolayer adsorption occurs at low relative pressure range. At higher relative pressure range ( $P/P_0 > 0.7$ ), the hysteresis loop appears which is responsible for capillary condensation in the mesopores. The calculated BET surface area was found to be  $23.6 \text{ m}^2/\text{g}$ . The low surface area is due to high diameter and the presence of amorphous carbon coating (Fig. 2j) in the outer wall of as-prepared CNFs that decreases the porosity of CNFs which is well evident from TEM analysis.

#### Role of Sulfur for the Growth of Carbon Nanofibers

The role of sulfur accompanied with transition metal catalyst (Fe, Ni) for the formation of carbon nanofibers has been observed by several groups [9, 11]. From Fe–S binary alloys phase diagram it is clear that solubility of sulfur in Fe is very low, while sulfur can partially react with Fe to form a FeS–Fe eutectic alloys phase and lower down the local region surface free energy for the catalytic formation



of CNFs than that of the bare  $\alpha$ -Fe phase. In our reaction condition we have shown the concentration dependent enhancement and poisoning of Fe catalyst particle in the growth process of carbon nanofiber by sulfur using turpentine oil as carbon precursor and ferrocene as a dissolved catalyst. It is well evident that CNFs are susceptible to nucleate and grow from the molten catalyst surface where sulfur of 42 at.% concentration effectively reacts with Fe particle to decrease the melting point of the local region around 980 °C which is very close to our reaction temperature. This molten state of metal particle catalytically enhances the dissolution of carbon atom leading to the high growth of fiber material through VLS mechanism. Catalytic enhancement of growth process with increasing sulfur concentration reduces the residence time which inhibit the non catalytic CVD coating or soot formation [9]. At low sulfur concentration (10.5 at.%) fiber growth is very less with lot of non-catalytic CVD coating or soot particles. In our experiment it has been observed that with 21 and 31.5 at.% of sulfur produces carbon nanofibers of higher yield compare to that of very low and very high concentration of sulfur. At these two intermediate concentration of sulfur (21 and 31.5 at.%), the surface of the as-grown carbon nanofibers are very smooth and some amount of amorphous carbon are occasionally observed which is in accordance with SEM, TEM and TGA/DTA analysis. The depression of freezing point of binary alloy system (Fe–S) has a linear relationship with concentration of sulfur up to a certain limit. The yield of the carbon nanofiber gradually increases with increasing sulfur concentration and reaches to a maxima at 31.5 at.% of sulfur. There is a steady fall of fiber growth rate at sulfur concentration of 40 at.%. In this case the amount of CNFs is very low, which is observed from SEM analysis. This clearly shows that not only the sulfur has the promoting effect for fiber grown over Fe catalyst but after a certain limiting concentration it acts as an inhibitor due to poisoning of catalyst leading to product of low yield.

## Conclusions

Carbon nanofibers with diameters 20–130 nm were grown successfully when turpentine oil containing ferrocene and sulfur was used as feedstock in the growth process. The morphology and yield of the as-grown CNFs strongly influenced by the concentration of the promoting agent. The results indicate that addition of sulfur to the ferrocene

catalyst can increase the yield of fiber. Optimum amount of sulfur have a promoting effect for the growth of CNFs. However, addition of large quantity of sulfur decreases the efficiency of the catalyst and only a few CNFs were formed. In our case, the best results we obtained with sulfur atomic concentration of 31.5 at.%. The result shows that turpentine oil is an ideal natural carbon feedstock for synthesis of CNF. The as-prepared CNFs of different morphologies may significantly contribute for their potential applications. The nanofibers containing sharp tip may exhibit enhanced field emission property and nanofibers with open ended is possibly benefit to the gas storage.

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